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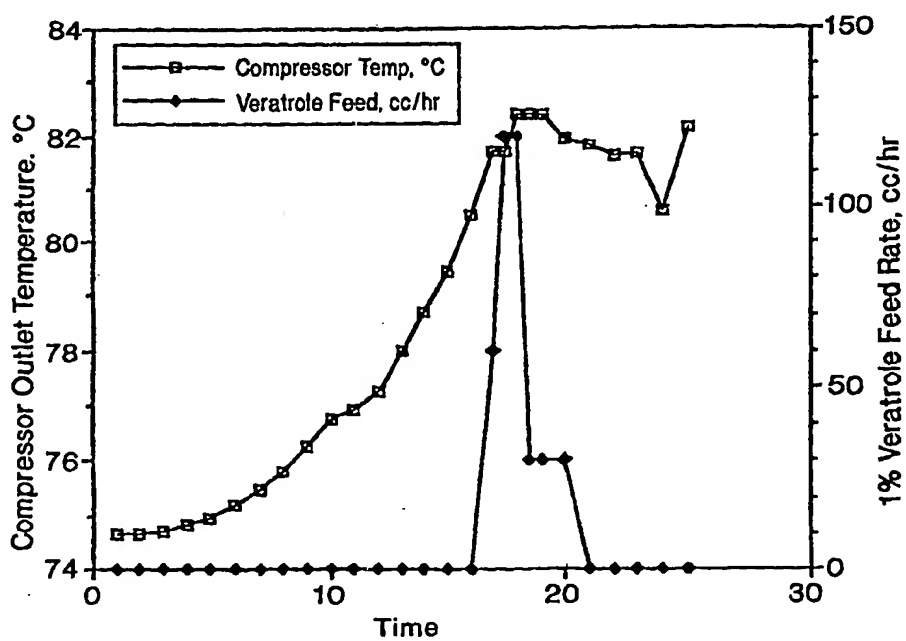
(54) Title: REDUCTION OF FOULING IN OLEFIN POLYMERIZATION SYSTEMS



(57) Abstract

A method of inhibiting polymer build–up in a polymerization system during polymerization of an olefin monomer into a polyolefin in the presence of an unsupported, liquid form catalyst composition comprising a single site catalyst and an activating cocatalyst is provided, which comprises introducing into the system an antifouling agent in an amount sufficient to inhibit polymer build–up.

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REDUCTION OF FOULING IN OLEFIN POLYMERIZATION SYSTEMS

The invention relates to the reduction of fouling during olefin polymerization, and particularly the reduction of fouling during olefin polymerization in the presence of an unsupported, liquid form catalyst composition comprising a single site catalyst.

BACKGROUND OF THE INVENTION

Olefin polymers can be produced using a variety of polymerization systems that involve solution, slurry, suspension, or gas phase polymerization. In commercial operation, these polymerization systems can operate for extended periods of time without major difficulty. A significant portion of the polyolefin patent literature discloses reaction conditions, methods of operation, and transition and reactor start-up procedures that provide good reactor performance.

Unfortunately, from time to time undesirable polymer deposits tend to build up on the reactor walls or in the recycle lines, heat exchangers, compressors, and other equipment. In polymerization systems employing gas phase, fluidized bed reactors for instance, these polymer deposits restrict the flow of recirculating gas through the system, eventually reducing the superficial gas velocity to such an extent that good fluidization of the bed cannot be maintained.

In the presence of single site catalysts, fouling in a polymerization system is often more severe than that seen with traditional Ziegler-Natta catalysts. Single site catalyst are catalytic compounds in which each catalyst molecule contains one or only a few polymerization sites. Single site catalysts have been shown to be highly useful in the preparation of

polyolefins, producing relatively homogeneous copolymers at good polymerization rates, allowing one to tailor closely the final properties of the polymer produced. Metallocenes are the most well known type of single site catalyst, and are organometallic coordination complexes containing one or more π-bonded moieties (i.e., cycloalkadienyl groups) in association with a metal atom from Groups IIIB to VIII or the Lanthanide series of the Periodic Table of Elements.

Compared with Ziegler-Natta catalysts, single site catalysts exhibit increased activity with increasing polymerization temperature and long catalyst lifetimes. In addition, olefin polymers made with single site catalysts can melt 10 to 20° C below the melting temperature of Ziegler-Natta-made polymers of the same density. Accordingly, polymerization systems are especially prone to fouling when catalyst compositions comprising single site catalysts are used.

It is known to use a number of antifouling agents in olefin polymerization systems employing conventional Ziegler-Natta catalysts such as titanium/magnesium/electron donor complexes that are typically activated with aluminum alkyl cocatalysts. It is also known to use antifouling agents in connection with supported catalyst compositions comprising metallocenes.

A need exists for a method of combating polymer build-up in olefin polymerization systems that utilize unsupported, liquid form catalyst compositions that comprise single site catalysts. Unsupported catalyst compositions are preferred from the standpoint of avoiding the disadvantages of supported catalyst compositions, such as extra cost and increased ash content in the finished polymer. However, fouling problems tend to be more severe in the presence of these, especially when they comprise single site catalysts. In connection with the present invention, it

has been found that fouling in the presence of unsupported, liquid form catalyst compositions comprising single site catalysts is particularly troublesome in the hottest sections of the polymerization system. In fluidized bed, gas phase reactors, such sections are the gas recycle line from the expanded section of the reactor to the compressor, the compressor itself, and the compressor discharge.

SUMMARY OF THE INVENTION

The invention provides a method of inhibiting polymer build-up in a polymerization system during polymerization of an olefin monomer into a polyolefin in the presence of an unsupported, liquid form catalyst composition comprising a single site catalyst and an activating cocatalyst, which comprises introducing into the system an antifouling agent in an amount sufficient to inhibit polymer build-up. Preferably, the antifouling agent is selected from the group consisting of 1,2-dimethoxybenzene and propylene glycol.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the effect of the addition of an antifouling agent to a gas phase polymerization system according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention is applicable to the polymerization of olefins by any suspension, solution, slurry, or gas phase process, using known equipment and reaction conditions, and is not limited to any specific type of

polymerization system. Generally, olefin polymerization temperatures range from about 0°C to about 200°C at atmospheric, subatmospheric, or superatmospheric pressures. Slurry or solution polymerization systems may utilize subatmospheric or superatmospheric pressures and temperatures in the range of about 40°C to about 110°C. A useful liquid phase polymerization system is described in U.S. Patent 3,324,095. Liquid phase polymerization systems generally comprise a reactor to which olefin monomer and catalyst composition are added, and which contains a liquid reaction medium for dissolving or suspending the polyolefin. The liquid reaction medium may consist of the bulk liquid monomer or an inert liquid hydrocarbon that is nonreactive under the polymerization conditions employed. Although such an inert liquid hydrocarbon need not function as a solvent for the catalyst composition or the polymer obtained by the process, it usually serves as solvent for the monomers employed in the polymerization. Among the inert liquid hydrocarbons suitable for this purpose are isopentane, hexane, cyclohexane, heptane, benzene, toluene, and the like. Reactive contact between the olefin monomer and the catalyst composition should be maintained by constant stirring or agitation. The reaction medium containing the olefin polymer product and unreacted olefin monomer is withdrawn from the reactor continuously. The olefin polymer product is separated, and the unreacted olefin monomer and liquid reaction medium are recycled into the reactor.

The invention is, however, especially useful with gas phase polymerization systems, with superatmospheric pressures in the range of 1 to 1000 psi, preferably 50 to 400 psi, most preferably 100 to 300 psi, and temperatures in the range of 30 to 130°C, preferably 65 to 110°C. Stirred or fluidized bed gas phase polymerization systems are particularly useful. Generally, a conventional gas phase, fluidized bed process is conducted by

passing a stream containing one or more olefin monomers continuously through a fluidized bed reactor under reaction conditions and in the presence of catalyst composition at a velocity sufficient to maintain a bed of solid particles in a suspended condition. A stream containing unreacted monomer is withdrawn from the reactor continuously, compressed, cooled, optionally partially or fully condensed, and recycled into the reactor. Product is withdrawn from the reactor and make-up monomer is added to the recycle stream. As desired for temperature control of the polymerization system, any gas inert to the catalyst composition and reactants may also be present in the gas stream. In addition, a fluidization aid such as carbon black, silica, clay, or talc may be used, as disclosed in U.S. Patent No. 4,994,534.

The polymerization system may comprise a single reactor or in two or more reactors in series, and is conducted substantially in the absence of catalyst poisons. Organometallic compounds may be employed as scavenging agents for poisons to increase the catalyst activity. Examples of scavenging agents are metal alkyls, preferably aluminum alkyls, most preferably triisobutylaluminum.

Conventional adjuvants may be used in the process, provided they do not interfere with the operation of the catalyst composition in forming the desired polyolefin. Hydrogen may be used as a chain transfer agent in the process, in amounts up to about 10 moles of hydrogen per mole of total monomer feed.

Polyolefins that may be produced according to the invention include, but are not limited to, those made from olefin monomers such as ethylene and linear or branched higher alpha-olefin monomers containing 3 to about 20 carbon atoms. Homopolymers or interpolymers of ethylene and such higher alpha-olefin monomers, with densities ranging from about 0.86 to

about 0.95 may be made. Suitable higher alpha-olefin monomers include, for example, propylene, 1-butene, 1-pentene, 1-hexene. 4-methyl-1-pentene, 1-octene, and 3,5,5-trimethyl-1-hexene. Olefin polymers according to the invention may also be based on or contain conjugated or non-conjugated dienes, such as linear, branched, or cyclic hydrocarbon dienes having from about 4 to about 20, preferably 4 to 12, carbon atoms. Preferred dienes include 1,4-pentadiene, 1,5-hexadiene, 5-vinyl-2-norbornene, 1,7-octadiene, vinyl cyclohexene, dicyclopentadiene, butadiene, isobutylene, isoprene, ethylidene norbornene and the like. Aromatic compounds having vinyl unsaturation such as styrene and substituted styrenes. and polar vinyl monomers such as acrylonitrile, maleic acid esters, vinyl acetate, acrylate esters, methacrylate esters, vinyl trialkyl silanes and the like may be polymerized according to the invention as well. Specific polyolefins that may be made according to the invention include, for example, polyethylene, polypropylene, ethylene/propylene rubbers (EPR's), ethylene/propylene/diene terpolymers (EPDM's), polybutadiene, polyisoprene and the like.

The present invention is useful with unsupported, liquid form catalyst compositions comprising a single site catalyst and an activating cocatalyst. One or more than one single site catalyst and activating cocatalyst may be employed in the catalyst composition.

The catalyst composition is introduced into the reaction zone in unsupported, liquid form, for example as described in U.S. Patent 5,317,036. As used herein, "unsupported, liquid form" includes liquid catalyst, liquid cocatalyst, solution(s) or dispersions of catalyst and cocatalyst in the same or different solvent(s), and combinations thereof. Unsupported, liquid form catalyst compositions have a number of practical benefits. Unsupported catalyst compositions avoid the costs associated with support material and

its preparation, and the provide for the realization of a very high catalyst surface area to volume ratio. Furthermore, unsupported catalyst compositions produce polymers having a much lower residual ash content than polymers produced using supported catalyst compositions.

The single site catalyst may be a metallocene, i.e., an organometallic coordination complex of one or more π-bonded moieties in association with a metal atom from groups IIIB to VIII or the rare earth metals of the Periodic Table. Bridged and unbridged mono-, di-, and tri-cycloalkadienyl/metal compounds are the most common metallocene catalysts, and generally are of the formula:

$$(L)_y R^1_z (L')MX_{(x-y-1)} \qquad (I)$$

wherein M is a metal from groups IIIB to VIII or a rare earth metal of the Periodic Table; L and L' are the same or different and are π-bonded ligands coordinated to M, preferably cycloalkadienyl groups such as cyclopentadienyl, indenyl, or fluorenyl groups optionally substituted with one or more hydrocarbyl groups containing 1 to 20 carbon atoms; R^1 is selected from the group consisting of C_1-C_4 substituted or unsubstituted alkylene radicals, dialkyl or diaryl germanium or silicon groups, and alkyl or aryl phosphine or amine radicals bridging L and L'; each X is independently hydrogen, an aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having 1-20 carbon atoms, a hydrocarboxy radical having 1-20 carbon atoms, or a halogen; n and m are each 0, 1, 2, 3, or 4; y is 0, 1, or 2; x is 1, 2, 3, or 4 depending upon the valence state of M; z is 0 or 1 and is 0 when y is 0; and x-y ≥ 1.

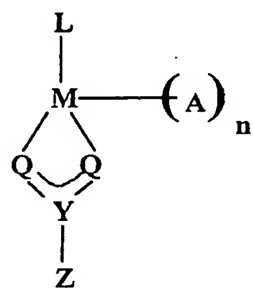
Illustrative but non-limiting examples of metallocenes represented by formula I are dialkyl metallocenes such as bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopenta-dienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium methyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopentadienyl)zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)-vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide; the trialkyl metallocenes such as cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl, cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl, and cyclopentadienyl hafnium trimethyl; monocyclopentadienyl titanocenes such as pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride, bis(pentamethylcyclopentadienyl) titanium diphenyl; the carbene represented by the formula bis(cyclopentadienyl)titanium=CH2 and derivatives of this reagent; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, trialkyl, tetra-alkyl and penta alkyl cyclopentadienyl titanium compounds such as

bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride; silicon, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes, and the like; as well as bridged metallocenes such as isopropyl(cyclopentadienyl)(fluorenyl)zirconium dichloride, isopropyl(cyclopentadienyl) (octahydrofluorenyl)zirconium dichloride, diphenylmethylene(cyclopentadienyl)(fluorenyl) zirconium dichloride, diisopropylmethylene (cyclopentadienyl)(fluorenyl)-zirconium dichloride, diisobutylmethylene(cyclopentadienyl)(fluorenyl) zirconium dichloride, ditertbutylmethylene (cyclopentadienyl)-(fluorenyl)zirconium dichloride, cyclohexylidene(cyclopentadienyl)-(fluorenyl) zirconium dichloride, diisopropylmethylene (2,5-dimethylcyclopentadienyl)(fluorenyl)zirconium dichloride, isopropyl(cyclopentadienyl)(fluorenyl) hafnium dichloride, diphenylmethylene (cyclopentadienyl) (fluorenyl)hafnium dichloride, diisopropylmethylene(cyclopentadienyl) (fluorenyl)hafnium dichloride, diisobutylmethylene(cyclopentadienyl) (fluorenyl)hafnium dichloride, ditertbutylmethylene(cyclopentadienyl) (fluorenyl)hafnium dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride, diisopropylmethylene(2,5-dimethylcyclopentadienyl) (fluorenyl)-hafnium dichloride, isopropyl(cyclopentadienyl)(fluorenyl)titanium dichloride, diphenylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, diisopropylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, diisobutylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, ditertbutylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, cyclohexylidene(cyclopentadienyl) (fluorenyl)titanium dichloride,

diisopropylmethylene(2,5 dimethylcyclopentadienyl fluorenyl)titanium dichloride, racemic-ethylene bis (1-indenyl) zirconium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (4,5,6,7- tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2- tetramethylsilanylene bis (1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1- indenyl) zirconium (IV), dichloride, ethylidene (1-indenyl tetramethylcyclopentadienyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (2-methyl-4-t-butyl-1-cyclopentadienyl) zirconium (IV) dichloride, racemic-ethylene bis (1-indenyl) hafnium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) hafnium (IV) dichloride, racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1- indenyl) hafnium (IV) dichloride, racemic-1,1,2,2- tetramethylsilanylene bis (1-indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV), dichloride, ethylidene (1-indenyl-2,3,4,5- tetramethyl-1-cyclopentadienyl) hafnium (IV) dichloride, racemic- ethylene bis (1-indenyl) titanium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) titanium (IV) dichloride racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) titanium IV) dichloride.

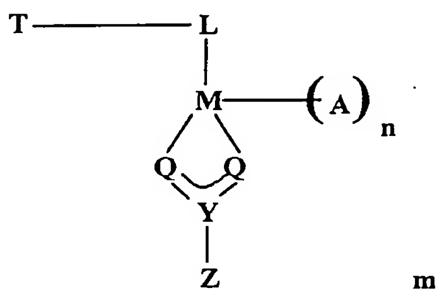
A preferred class of single site catalyst is complexes of transition metals, substituted or unsubstituted π-bonded ligands, and heteroallyl

moieties, such as those described in U.S. Patent No. 5,527,752. Preferably, such complexes have one of the following formulas (II or III):



(II)

or



(III)

wherein:

M is a transition metal, preferably Zr or Hf;

L is a substituted or unsubstituted, π-bonded ligand coordinated to M, preferably a substituted cycloalkadienyl ligand;

each Q is independently selected from the group consisting of -O-, -NR^3-, -CR^3_2- and -S-, preferably oxygen;

Y is either C or S, preferably carbon;

Z is selected from the group consisting of -OR^3, -$NR^3{}_2$, -$CR^3{}_3$, -SR^3, -$SiR^3{}_3$, -$PR^3{}_2$, and -H, with the proviso that when Q is -NR^3 then Z is selected from the group consisting of -OR^3, -$NR^3{}_2$, -SR^3, -$SiR^3{}_3$, -$PR^3{}_2$, and -H, preferably Z is selected from the group consisting of -OR^3, -$CR^3{}_3$, and -$NR^3{}_2$;

n is 1 or 2;

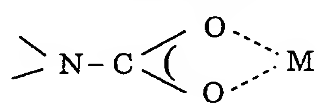
A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1, preferably A is a carbamate, carboxylate or other heteroallyl moiety described by Q, Y and Z combination; and

each R^3 is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus and one or more R^3 groups may be attached to the L substituent, preferably R^3 is a hydrocarbon group containing from 1 to 20 carbon atoms, most preferably an alkyl, cycloalkyl or an aryl group;

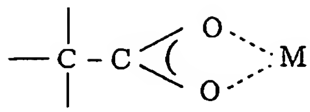
T is a bridging group selected from the group consisting of alkylene or arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone or alkyl phosphine; and

m is 2 to 7, preferably 2 to 6, most preferably 2 or 3.

The supportive substituent formed by Q, Y and Z is a unicharged polydentate ligand exerting electronic effects due to its high polarizability, similar to the cyclopentadienyl group. In the most preferred embodiments of this invention, the disubstituted carbamates,



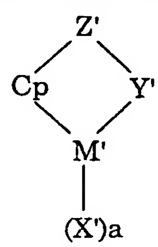
and the carboxylates



are employed.

Examples of single site catalysts according to formulas II and III include indenyl zirconium tris(diethylcarbamate), indenyl zirconium tris(trimethylacetate), indenyl zirconium tris(p-toluate), indenyl zirconium tris(benzoate), (1-methylindenyl)zirconium tris(pivalate), (2-methylindenyl) zirconium tris(diethylcarbamate), (methylcyclopentadienyl) zirconium tris(pivalate), cyclopentadienyl tris(pivalate), and (pentamethylcyclopentadienyl) zirconium tris(benzoate). Preferred examples of these single site catalysts are indenyl zirconium tris(diethylcarbamate) and indenyl zirconium tris(trimethylacetate).

Another type of single site catalyst that can be used in accordance with the invention is a constrained geometry catalyst of the formula:



(IV)

wherein:

M' is a metal of groups IIIB to VIII of the Periodic Table;

Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonded mode to M';

Z' is a moiety comprising boron, or a member of group IVB of the Periodic Table and optionally sulfur or oxygen, the moiety having up to 20 non-hydrogen atoms, and optionally Cp and Z' together form a fused ring system;

X' is an anionic ligand group or a neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

a is 0, 1, 2, 3 or 4 depending on the valence of M'; and

Y' is an anionic or non-anionic ligand group bonded to Z' and M' and is nitrogen, phosphorus, oxygen or sulfur having up to 20 non-hydrogen atoms, and optionally Y' and Z' together form a fused ring system.

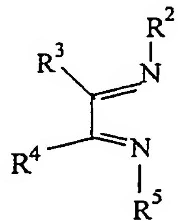
Constrained geometry catalysts are well known to those skilled in the art and are disclosed in, for example, U.S. Patent Nos. 5,026,798 and 5,055,438 and published European Application No. 0 416 815 A2.

Illustrative but non-limiting examples of substituents Z', Cp, Y', X' and M' in formula IV are:

Z'	Cp	Y'	X'	M'
dimethyl-silyl	cyclopenta-dienyl	t-butylamido	chloride	titanium
methyl-phenylsilyl	fluorenyl	phenylamido	methyl	zirconium
diphenyl-silyl	indenyl	cyclohexylamido		hafnium
tetramethyl-ethylene		oxo		
ethylene	tetramethyl-cyclopenta-dienyl			
diphenyl-methylene				

The invention is also useful with a third class of single site catalyst, di(imine) metal complexes, as described in PCT Application No. WO

96/23010. Such di(imine) metal complexes are transition metal complexes of bidentate ligands selected from the group consisting of



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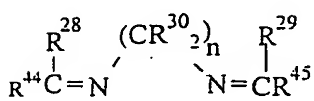

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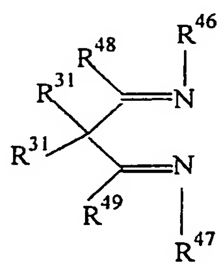

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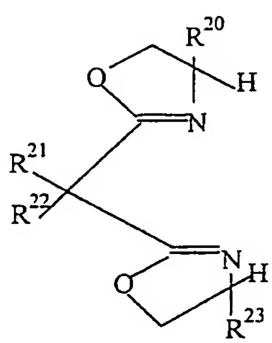


(VIII)

wherein said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni, and Pd;

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

each R^{31} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

n is 2 or 3;

and provided that:

said transition metal also has bonded to it a ligand that may be displaced by or added to the olefin monomer being polymerized; and

when the transition metal is Pd, said bidentate ligand is (V), (VII) or (VIII).

The activating cocatalyst is capable of activating the single site catalyst. Preferably, the activating cocatalyst is one of the following: (a) branched or cyclic oligomeric poly(hydrocarbyl-aluminum oxide)s which contain repeating units of the general formula $-(Al(R^*)O)-$, where R^* is hydrogen, an alkyl radical containing from 1 to about 12 carbon atoms, or an aryl radical such as a substituted or unsubstituted phenyl or naphthyl group; (b) ionic salts of the general formula $[A^+][BR^{**}{}_4{}^-]$, where A^+ is a cationic Lewis or Bronsted acid capable of abstracting an alkyl, halogen, or hydrogen from the metallocene catalysts, B is boron, and R^{**} is a substituted aromatic hydrocarbon, preferably a perfluorophenyl radical; and (c) boron alkyls of the general formula $BR^{**}{}_3$, where R^{**} is as defined above.

Preferably, the activating cocatalyst is an aluminoxane such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), or a boron alkyl. Aluminoxanes are preferred and their method of preparation is well known in the art. Aluminoxanes may be in the form of oligomeric linear alkyl aluminoxanes represented by the formula:

$$R^{***}\left(\begin{array}{c}-Al-O-\\ |\\ R^{***}\end{array}\right)_s AlR^{***}{}_2$$

or oligomeric cyclic alkyl aluminoxanes of the formula:

$$\left(\begin{array}{c} \text{-Al-O-} \\ | \\ R^{***} \end{array} \right)_p$$

wherein s is 1-40, preferably 10-20; p is 3-40, preferably 3-20; and R*** is an alkyl group containing 1 to 12 carbon atoms, preferably methyl or an isobutyl radical such as a substituted or unsubstituted or radical.

The amount of activating cocatalyst and single site catalyst in the catalyst composition, whether the catalyst composition is formed in situ as it is being introduced into the reaction zone or formed prior to introduction into the reaction zone, can vary over a wide range. When the cocatalyst is a branched or cyclic oligomeric poly(hydrocarbylaluminum oxide), the mole ratio of aluminum atoms contained in the poly(hydrocarbylaluminum oxide) to metal atoms contained in the single site catalyst is generally in the range of from about 2:1 to about 100,000:1, preferably in the range of from about 10:1 to about 10,000:1, and most preferably in the range of from about 50:1 to about 2,000:1. When the cocatalyst is an ionic salt of the formula $[A^+][BR^*{}_4{}^-]$ or a boron alkyl of the formula $BR^*{}_3$, the mole ratio of boron atoms contained in the ionic salt or the boron alkyl to metal atoms contained in the single site catalyst is generally in the range of from about 0.5:1 to about 10:1, preferably in the range of from about 1:1 to about 5:1.

According to the invention, polymer build-up or fouling in an olefin polymerization system employing a catalyst composition described above may be inhibited by introducing into the polymerization system an antifouling agent. Examples of antifouling agents include hydrogen,

oxygen, water, ethers, alcohols. ketones, aldehydes. carboxylic acids, esters, carbonates, phosphines, phosphine oxides, phosphates, phosphites, amines, amides, nitriles, alkoxy silanes, aluminum alkoxides, nitric oxides, carbon oxides, sulfur oxides, and the like.

Ethers include aliphatic ethers, cycloaliphatic ethers, aromatic ethers, monoethers, diethers, tetraethers, polyethers, and the like. Particularly useful ethers are aliphatic monoethers, and cycloaliphatic monoethers containing from 2 to 20 carbon atoms. Other particularly useful ethers are aliphatic diethers. and cycloaliphatic diethers containing from 3 to 20 carbon atoms. Still other particularly useful ethers are aromatic ethers, aliphatic triethers, and aliphatic tetraethers containing from 7 to 20 carbon atoms. Preferred ethers are dimethyl ether, diethyl ether, tetrahydrofuran, dioxane, 2,5,8,11,14-pentaoxopentadecane, methoxy benzene, and 1,2-dimethoxy ethane, and 1,2-dimethoxybenzene, commercially available from Fluka Chemical under the tradename Veratrole®.

Alcohols include mono alcohols, glycols, triols, and polyols. Particularly useful alcohols include aliphatic alcohols containing from 1 to 20 carbon atoms, glycols containing from 2 to 20 carbon atoms, aromatic alcohols and cycloaliphatic alcohols containing from 6 to 20 carbon atoms. Preferred alcohols are methyl alcohol, ethyl alcohol, 2-ethyl-1-hexanol, cyclohexanol, ethylene glycol, glycerine, phenol, and propylene glycol.

Particularly useful ketones are aliphatic monoketones, cycloaliphatic monoketones, and cycloaliphatic diketones containing from 3 to 20 carbon atoms. Other particularly useful ketones are aromatic ketones containing from 8 to 20 carbon atoms and aliphatic diketones containing from 5 to 20 carbon atoms. Preferred ketones are acetone, cyclohexanone, 1,4-cyclohexanedione. acetophenone, benzophenone, acetylacetone, and diethyl ketone.

Particularly useful aldehydes are aliphatic aldehydes containing from 2 to 20 carbon atoms and aromatic aldehydes containing from 7 to 20 carbon atoms. Preferred aldehydes are acetaldehyde and benzaldehyde.

Particularly useful esters are aliphatic monoesters, cycloaliphatic monoesters, and cycloaliphatic diesters containing from 3 to 20 carbon atoms. Other particularly useful esters are aromatic esters containing from 8 to 20 carbon atoms and aliphatic diesters containing from 5 to 20 carbon atoms. Preferred esters are methyl acetate, ethyl acetate, e-caprolactone, methyl benzoate, diisobutylphthalate, and dimethyl malonate.

Particularly useful aldehydes are aliphatic aldehydes containing from 2 to 20 carbon atoms and aromatic aldehydes containing from 7 to 20 carbon atoms. Preferred aldehydes are acetaldehyde and benzaldehyde.

Particularly useful carboxylic acids are aliphatic carboxylic acids containing from 2 to 20 carbon atoms and aromatic carboxylic acids containing from 7 to 20 carbon atoms. Preferred carboxylic acids are acetic acid and benzoic acid.

Particularly useful carbonates are aliphatic and cycloaliphatic carbonates containing from 3 to 20 carbon atoms. Preferred carbonates are dimethyl carbonate, diethyl carbonate, and 1,3-dioxolan-2-one, and para ethyl ethoxybenzoate (PEEB).

Particularly useful phosphines, phosphine oxides, phosphates, and phosphites contain aliphatic moieties with from 1 to 12 carbon atoms, aromatic moieties with from 6 to 12 carbon atoms, cycloaliphatic moieties with from 4 to 12 carbon atoms, and mixtures thereof. Preferred phosphines, phosphine oxides, phosphates, and phosphites are trimethyl phosphine, triisopropyl phosphine, triphenyl phosphine, tricyclohexyl phosphine, trimethyl phosphine oxide, triisopropyl phosphine oxide, triphenyl phosphine oxide, tricyclohexyl phosphine oxide, trimethyl

phosphate, triisopropyl phosphate, triphenyl phosphate, tricyclohexyl phosphate, trimethyl phosphite, triisopropyl phosphite, triphenyl phosphite, and tricyclohexyl phosphite.

Particularly useful amines and amides contain hydrogen, aliphatic moieties with from 1 to 30 carbon atoms, aromatic moieties with from 6 to 20 carbon atoms, cycloaliphatic moieties with from 4 to 20 carbon atoms, and mixtures thereof. Preferred amines and amides are trimethyl amine, triisopropyl amine, triphenyl amine, tricyclohexyl amine, N, N-dimethyl analine, N-ethylacetamide, N, N-dimethylbenzamide, acetanalide, and N,N-bis(2-hydroxyethyl)alkylamine, especially N,N-bis(2-hydroxyethyl)alkylamine.

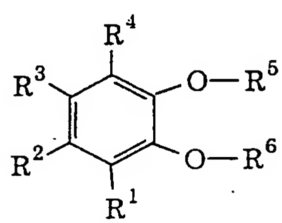
Particularly useful nitriles contain aliphatic moieties with from 1 to 12 carbon atoms, aromatic moieties with from 6 to 12 carbon atoms, and cycloaliphatic moieties with from 4 to 12 carbon atoms. Preferred nitriles are acetonitrile and benzonitrile.

Particularly useful alkoxy silanes contain hydrogen, aliphatic moieties with from 1 to 12 carbon atoms, aromatic moieties with from 6 to 12 carbon atoms, cycloaliphatic moieties with from 4 to 12 carbon atoms, and mixtures thereof. Preferred alkoxy silanes are phenyltrimethoxysilane, n-propyltrimethoxysilane, cyclohexyltrimethoxysilane, cyclohexyltriethoxysilane, diphenyldimethoxysilane, disobutyldimethoxysilane, di*t*-butyldimethoxysilane, and di*t*-butyldiethoxysilane.

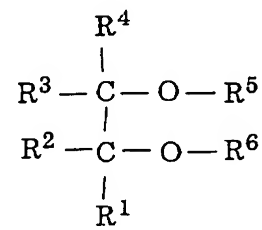
Particularly useful aluminum alkoxides contain aliphatic moieties with from 1 to 12 carbon atoms, aromatic moieties with from 6 to 12 carbon atoms, cycloaliphatic moieties with from 4 to 12 carbon atoms, and mixtures thereof. Preferred aluminum alkoxides are diethylaluminum ethoxide,

diisobutylaluminum ethoxide, diisobutylaluminum isobutoxide, diphenylaluminum ethoxide, and dicyclohexylaluminum ethoxide.

In a highly preferred embodiment of the invention the antifouling agent has the following formula:



or



wherein R^1, R^2, R^3, R^4, R^5 and R^6 are the same or different and are H, linear or branched alkyl radicals having from 1-20 carbon atoms, cycloalkyl, aryl, or arylalkyl, which, with the exception of H, can combine to form rings of cyclic alkyl or benzene; or R^5 and R^6 can combine to form a divalent hydrocarbon radical containing from 1-20 carbon atoms.

Most preferably, the antifouling agent is selected from the group consisting of 1,2-dimethoxybenzene and propylene glycol.

The antifouling agent can be introduced at a variety of locations in the polymerization system, such as into the reaction zone, the recycle line, upstream of heat exchangers or compressors, i.e., specific equipment prone to foul, or into the catalyst composition delivery equipment, for example a nozzle for spraying unsupported, liquid form catalyst or cocatalyst or both into the reaction zone. The antifouling agent can be added to the polymerization system with activators, scavengers, promoters, or inhibitors.

For a fluidized bed, gas phase reactor, the antifouling agent can be introduced into the expanded section, fluid bed, or below the distributor plate, to product receiving or resin handling vessels connected to the reactor,

to cyclones, to resin containing vessels. reactors or transfer piping associated with the polymerization system, to instrument taps that purge into the polymerization system, into monomer, hydrogen, or other gaseous or liquid feeds going to the reactor, into liquid induced condensing agent feeds going to the reactor, into condensed liquid separated from the recycle gas in the recycle loop, into gases or liquids recycled to the reactor, to gases or liquids injected into the fluid bed above the distributor plate or through channels or ducts along the wall of the reactor within the fluid bed.

As required, one or more antifouling agents can be simultaneously added to the reactor at one or more locations, i.e., to the expanded section and before the recycle compressor. The antifouling agent can be added continuously or intermittently to the reactor as required to control fouling, which can be monitored by pressure drops across specific pieces of equipment such as a length of pipe in the recirculation line. Several hours may elapse between the intermittent feeds of antifouling agent, since it can provide extended protection against fouling.

The antifouling agent may be added to the polymerization system by a variety of methods, depending upon the polymerization system and the form of the antifouling agent. It may be added in neat or as a dilute solution. Depending upon the solubility of the antifouling agent, appropriate diluents may include olefin monomer or a hydrocarbon such as toluene or isopentane. The antifouling agent can be added as a gas, liquid, or solid. The antifouling agent can be added adsorbed on or dispersed with a fluidization aid such as carbon powder or calcined silica that is added intermittently or continuously to the reactor. The antifouling agent may also be adsorbed on a support such as silica or granular polyolefin resin and added to the reactor.

The amount of antifouling agent that is introduced into the polymerization system to inhibit polymer build up is dependent on a number of factors, including the nature of the antifouling agent, the catalyst, the cocatalyst, the reaction temperature, the molar ratio of catalyst to cocatalyst, and the olefins present and their concentration. Preferably, the amount of antifouling agent that is introduced into the polymerization system ranges from about 0.01 to about 1000 parts per million by weight (ppmw) of the polyolefin produced, more preferably from about 0.05 to about 50 ppmw of the polyolefin produced. This ensures good antifouling protection without excessive loss of catalyst productivity.

In a preferred embodiment of the invention, polymerization is conducted in the gas phase in a fluidized bed reactor in the presence of an unsupported catalyst composition comprising a catalyst of formula II or III above and an aluminoxane cocatalyst along with an antifouling agent selected from the group consisting of 1,2-dimethoxybenzene and propylene glycol.

The disclosures of the patents and articles referred to above are incorporated herein by reference.

The following examples further illustrate the invention.

EXAMPLE 1

In this example Verotrole® (1,2-dimethoxybenzene), commercially available from Fluka Chemicals, was used to inhibit polymer build-up in a gas phase, fluidized bed reactor without a distributor plate producing an ethylene/hexene copolymer.

An 18-inch, carbon steel, pilot-scale, fluidized bed reactor was cleaned and brought up to the following polymerization conditions:

Temp:	60°C
Pressure:	348 psig
Ethylene Pressure:	142 psig
C_6/C_2 Mole Ratio:	0.017
Isopentane Conc.:	2.7 mole%
Dew Point:	25°C
Gas Velocity:	1.2 ft/sec

Indenyl zirconium tris(trimethylacetate) and modified methylaluminoxane (Type 3A commercially available from Akzo-Nobel) were premixed and fed to the reactor using isopentane as a carrier fluid through an internal mixing head atomization nozzle at the bottom of the reactor where the cycle gas entered. The polymer bed extended into the conical transition section of the reactor from the cycle piping inlet to the reactor bed wall. The flow of cycle gas into the transition section created a gas region into which the catalyst was sprayed. A 1.5 inch long nozzle, tube machined to a tapered point with an orifice at the end was fit over the internal mixing head and was used to feed the catalyst composition to the reactor. The nozzle tip extended about 3 to 4 inches into the transition cone and the full recycle gas flow of about 14,000 lb/hr flowed around it. Approximately 10 lb/hr of nitrogen was also supplied to the nozzle as an atomizing fluid.

The compressor outlet temperature began to increase about 3 to 4 hours after the reaction started as shown in Figure 1, which is a plot of the compressor outlet temperature and Veratrole feed rate versus time. This indicated fouling had occurred in the cycle line downstream of the

compressor or in the compressor case. By the end of about 16 hours, the compressor outlet temperature had increased by 8°C to about 82°C. Pressure drop across the heat exchanger remained about 4 inches of water during this time, which is typical.

A one wt% solution feed of Veratrole in isopentane was fed at 160 cc/hr into an elbow of the recycle line at the top of the reactor about 16 hours into the run. It entered through a 1/8 inch stinger inserted down vertically about two inches into the pipe. As shown in Figure 1, the compressor outlet temperature and associated fouling immediately stabilized.

The amount of Veratrole added caused the reaction to die back by about 50% within four hours. Accordingly, the reactor was purged with nitrogen to remove the Veratrole. MMAO was fed to the reactor during part of the purging to consume excess Veratrole.

Conditions for polymerization were reestablished. The compressor outlet increased from about 82 to 84°C as the reaction recovered. Veratrole was then fed again, this time as a 0.033 wt% solution in isopentane, at 50 cc/hr. The compressor outlet temperature stabilized at 84°C. Over the next 20 hours, the compressor outlet temperature dropped steadily to about 82°C. The heat exchanger pressure drop remained stable in the 4 to 5 psi range. Catalyst productivity was retarded by about 20%.

Fouling of the cycle line downstream of the Veratrole injection point was arrested, but the reactor experienced loss of cycle gas flow throughout the run. Compensatory opening of the cycle gas control valve maintained the flow at 1.2 ft/sec until the valve was fully opened. Flow then dropped to about 0.8 ft/sec within a couple of hours and the reactor was shut down and opened for inspection. Total run length was about two days not including the time that the reactor was purged.

Blockage occurred in the cycle line at the top of the reactor in the 8 to 9 inches of piping upstream from the point of Veratrole addition. The fouling observed in the compressor case, discharge and heat exchanger was thought to be due to operation without Veratrole. For the run length, the fouling was much reduced. Fouling at the discharge consisted of only a series of small transverse ridges across the top and bottom of the two inch pipe. Lightly sintered fines deposited on the heat exchanger tube sheet and the holes were clear. Without the addition of an antifouling agent, the discharge piping transverse ridges can be up to half the pipe diameter. In addition, some holes in the heat exchanger become blocked and polymer fouls the inner surface of the heat exchanger tubes.

EXAMPLE 2

Example 1 was repeated except that the 1/8 inch stinger introducing the Veratrole was extended further into the cycle piping about 2 inches into the top of the expanded section of the reactor. Veratrole was introduced as a 0.01 wt% solution in isopentane. The reactor start-up, catalyst composition and its feed system, and reaction conditions were similar to that in Example 1.

Veratrole addition began two hours after the catalyst composition was started. The Veratrole flow rate was 80 to 100 cc/hr for five hours and then discontinued when the catalyst productivity was about 50% of normal. Compressor outlet temperature and heat exchanger pressure drop were steady at about 75°C and 5.3 psi, respectively.

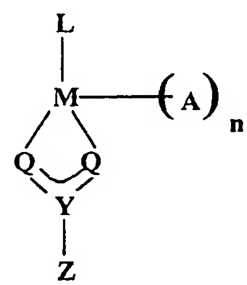
Resumption of Veratrole addition at 50 to 70 cc/hr decreased the catalyst productivity by about 15%. The compressor outlet temperature increased to 77.4°C over the next 18 hours of Veratrole addition. The heat exchanger pressure drop increased from 6.1 to 6.3 during the first 16 hours

of this period, and then increased suddenly to 7.0 as if small debris had lodged on the tube sheet. The reactor was shut down.

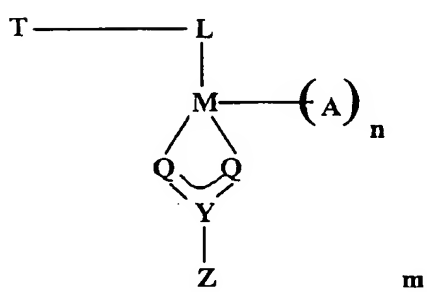
The cycle line, compressor and heat exchanger were essentially clean and did not require cleaning prior to the next polymerization run. The entrance to the cycle line that had plugged in Example 1 was clear except for a thin layer of polymer about 1/16 to 1/8 inch thick that extended around half the 3 inch pipe perimeter and about 2 inches in height from the expanded section back into the pipe. The stinger extending through the pipe was found to be off-center, favoring the side of the pipe that was clear.

We claim:

1. A method of inhibiting polymer build-up in gas phase polymerization system comprising a fluidized bed reactor during polymerization of an olefin monomer into a polyolefin in the presence of an unsupported, liquid form catalyst composition comprising a single site catalyst having the formula:



or



wherein:

M is a transition metal;

L is a substituted or unsubstituted, ¹-bonded ligand coordinated to M;

each Q is independently selected from the group consisting of -O-, -NR^3-, -CR^3_2- and -S-;

Y is C or S;

Z is selected from the group consisting of -OR^3, -NR^3_2, -CR^3_3, -SR^3, -SiR^3_3, -PR^3_2, and -H, with the proviso that when Q is -NR^3- then Z is selected from the group consisting of -OR^3, -NR^3_2, -SR^3, -SiR^3_3, -PR^3_2, and -H;

n is 1 or 2;

A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1; and

each R^3 is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus and one or more R^3 groups may be attached to the L substituent;

T is a bridging group selected from the group consisting of alkylene or arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone, and alkyl phosphine; and

m is 2 to 7,

and an aluminoxane cocatalyst, which comprises introducing into the system an antifouling agent selected from the group consisting of 1,2-dimethoxybenzene and propylene glycol.

2. The method of claim 1, wherein the single site catalyst is selected from the group consisting of indenyl zirconium tris(diethylcarbamate) and indenyl zirconium tris(trimethylacetate).

3. The method of claim 1, wherein the antifouling agent is introduced into the polymerization system by adding the antifouling agent to a recycle line of the polymerization system.

4. The method of claim 1, wherein the fluidized bed reactor has an expanded section and the antifouling agent is added to the expanded section.

5. A method of inhibiting polymer build-up in a polymerization system during polymerization of an olefin monomer into a polyolefin in the presence of an unsupported, liquid form catalyst composition comprising a single site catalyst and an activating cocatalyst, which comprises introducing into the system an antifouling agent in an amount sufficient to inhibit polymer build-up.

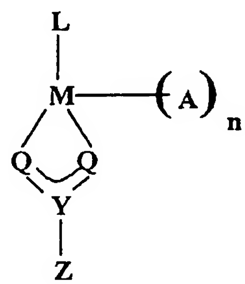
6. The method of claim 5, wherein the single site catalyst is metallocene of the formula:

$$(L)_y R^1_z (L')MX_{(x-y-1)}$$

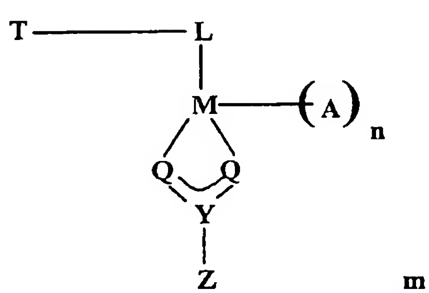
wherein M is a metal from groups IIIB to VIII or a rare earth metal of the Periodic Table; L and L' are the same or different and are π-bonded ligands coordinated to M; R^1 is selected from the group consisting of C_1-C_4 substituted or unsubstituted alkylene radicals, dialkyl or diaryl germanium or silicon groups, and alkyl or aryl phosphine or amine radicals; each X is independently hydrogen, an aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having 1-20 carbon atoms, a hydrocarboxy radical having 1-20 carbon atoms, or a halogen; n and m are each 0, 1, 2, 3, or 4; y is 0, 1, or 2; x

is 1, 2, 3, or 4 depending upon the valence state of M; z is 0 or 1 and is 0 when y is 0; and $x-y \geq 1$.

7. The method of claim 5, wherein the single site catalyst has the formula:



or



wherein:

M is a transition metal;

L is a substituted or unsubstituted, π-bonded ligand coordinated to M;

each Q is independently selected from the group consisting of -O-, -NR^3-, -$CR^3{}_2$- and -S-;

Y is C or S;

Z is selected from the group consisting of -OR^3, -$NR^3{}_2$, -$CR^3{}_3$, -SR^3, -$SiR^3{}_3$, -$PR^3{}_2$, and -H, with the proviso that when Q is -NR^3 then Z is selected from the group consisting of -OR^3, -$NR^3{}_2$, -SR^3, -$SiR^3{}_3$, -$PR^3{}_2$, and -H;

n is 1 or 2;

A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1; and

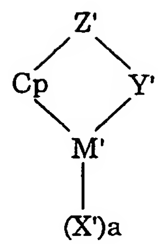
each R^3 is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus and one or more R^3 groups may be attached to the L substituent;

T is a bridging group selected from the group consisting of alkylene or arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone, or alkyl phosphine; and

m is 2 to 7.

8. The method of claim 7, wherein the single site catalyst is selected from the group consisting of indenyl zirconium tris(diethylcarbamate) and indenyl zirconium tris(trimethylacetate).

9. The method of claim 5, wherein the single site catalyst is a constrained geometry catalyst of the formula:



wherein:

M' is a metal of Groups IIIB to VIII of the Periodic Table;

Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonded mode to M';

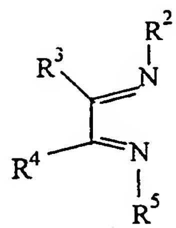
Z' is a moiety comprising boron, or a member of Group IVB of the Periodic Table and optionally sulfur or oxygen, the moiety having up to 20 non-hydrogen atoms, and optionally Cp and Z' together form a fused ring system;

X' is an anionic ligand group or a neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

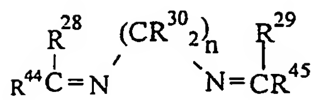
a is 0, 1, 2, 3 or 4 depending on the valence of M'; and

Y' is an anionic or non-anionic ligand group bonded to Z' and M' and is nitrogen, phosphorus, oxygen or sulfur having up to 20 non-hydrogen atoms, and optionally Y' and Z' together form a fused ring system.

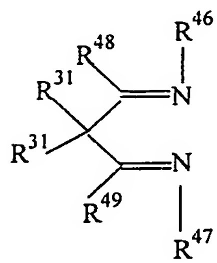
10. The method of claim 5, wherein the single site catalyst is a di(arylimine) metal complex comprising a transition metal and a bidentate ligand selected from the group consisting of:



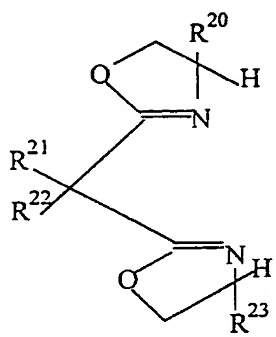
(V)



(VI)



(VII), and



(VIII)

wherein said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni, and Pd;

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

each R^{31} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

R^{21} and R^{22} are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

n is 2 or 3;

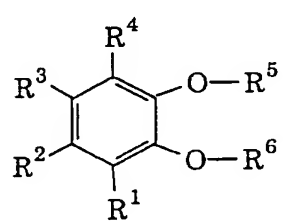
and provided that:

said transition metal also has bonded to it a ligand that may be displaced by or added to the olefinmonomer being polymerized; and

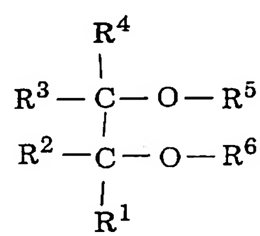
when the transition metal is Pd, said bidentate ligand is (V), (VII) or (VIII).

11. The method of claim 5, wherein the antifouling agent is selected from the group consisting of hydrogen, oxygen, water, ethers, alcohols, ketones, aldehydes, carboxylic acids, esters, carbonates, phosphines, phosphine oxides, phosphates, phosphites, amines, amides, nitriles, alkoxy silanes, aluminum alkoxides, nitric oxides, carbon oxides, and sulfur oxides.

12. The method of claim 5, wherein the antifouling agent has the formula:



or



wherein R^1, R^2, R^3, R^4, R^5, and R^6 are the same or different and are H, linear or branched alkyl radicals having from 1-20 carbon atoms, cycloalkyl, aryl, or arylalkyl, which, with the exception of H, can combine to form rings of cyclic alkyl or benzene; or R^5 and R^6 can combine to form a divalent hydrocarbon radical containing from 1-20 carbon atoms.

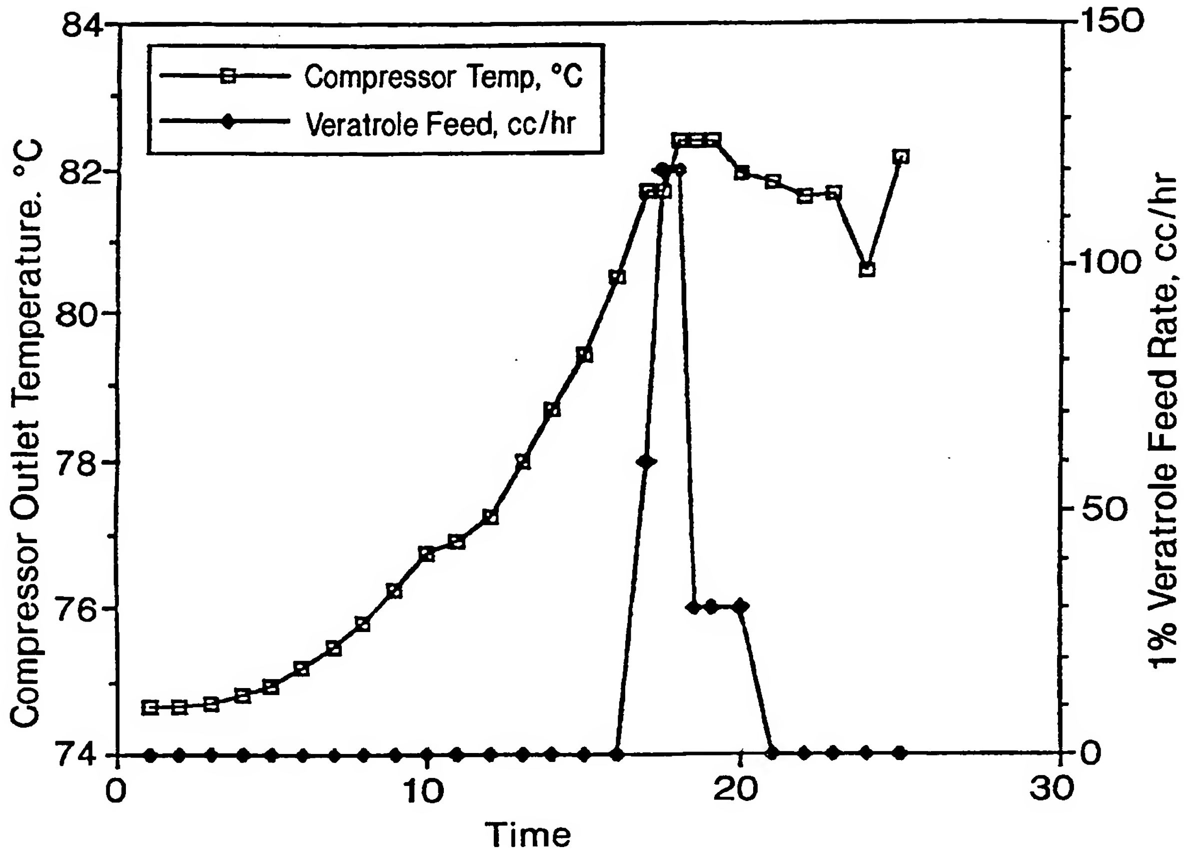
13. The method of claim 12, wherein the antifouling agent is selected from the group consisting of 1,2-dimethoxybenzene and propylene glycol.

14. The method of claim 5, wherein the amount of antifouling agent used is about 0.01 to about 1000 ppm by weight of the polyolefin.

15. The method of claim 5, wherein the antifouling agent is introduced into the polymerization system by adding the antifouling agent to a recycle line of the polymerization system.

16. The method of claim 5, wherein the polymerization is conducted in the gas phase.

17. The method of claim 16, wherein polymerization is conducted in a fluidized bed reactor having an expanded section and the antifouling agent is added to the expanded section.



84
82
80
78
76
74
150
100
50
0
0
10
20
30
Compressor Temp, °C
Veratrole Feed, cc/hr
Compressor Outlet Temperature. °C
1% Veratrole Feed Rate, cc/hr
Time

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/19073

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/00 C08F10/00 C08F2/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	see page 4, line 29 - line 51 see page 9, line 46 - page 10, line 10 see page 17, line 54 - line 56; claims	1-17
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Y	EP 0 359 444 A (BP CHEM INT LTD) 21 March 1990 see column 3, line 3 - line 42 see claims ---	1-17
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
12 January 1998	19/01/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kaumann, E

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International Application No
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